

Semi-local density functional for the exchange-correlation energy of electrons in two dimensions

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Abstract

We present a practical and accurate density functional for the exchange-correlation energy of electrons in two dimensions. The exchange part is based on a recent two-dimensional generalized-gradient approximation derived by considering the limits of small and large density gradients. The fully local correlation part is constructed following the Colle-Salvetti scheme and a Gaussian approximation for the pair density. The combination of these expressions is shown to provide an efficient density functional to calculate the total energies of two-dimensional electron systems such as semiconductor quantum dots. Excellent performance of the functional with respect to numerically exact reference data for quantum dots is demonstrated.

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1. INTRODUCTION

The practical capability of density-functional theory [1] (DFT) to capture many-particle properties of physically and chemically relevant systems crucially depends on the availability of good approximations for the exchange-correlation energy functional. Significant advances have been achieved by means of, e.g., local and semi-local approximations, orbital functionals, and hybrid functionals [2]. Most of these constructions have been carried out considering three spatial dimensions (3D) explicitly, which is natural in view of atoms, molecules, and solids. Consequently, however, the field of low-dimensional physics has been left, for the most part, outside the coverage of DFT. For example, density functionals developed particularly for 3D fail when applied to (quasi-)two-dimensional (2D) systems [4–6].

At present, 2D nanoscale structures have a rich variety including, e.g., quantum Hall bars, semiconductor quantum dots [3] and rings, and metal-oxide-semiconductor-based field-effect transistors [7]. It should be noted that the building block here is the *quasi-2D electron gas*, which can be treated, however, by a “pure” 2D approach, i.e., on a 2D grid with Coulombic electron-electron interactions. More explicitly, the degrees of freedom along the third dimension have been suppressed and the system is effectively 2D. Then, the influence of the surrounding host material is taken into account with the effective-mass approximation manifesting itself as an effective mass and a dielectric constant in the 2D Hamiltonian.

Within DFT, 2D systems are usually dealt with the 2D local-density approximation [8, 9] (LDA), which is accurate in terms of *total* energies in many cases [10, 11]. Problems are expected to arise in highly inhomogeneous systems, or when considering the very strong interaction regime [12], or close to dimensional crossovers [13]. Developments in 2D beyond the LDA have been carried out recently, leading to accurate density functionals for both exchange [13–16] and correlation [17, 18]. Good results have been obtained also from orbital functionals designed to follow the dimensional crossover [6], simple orbital-free total-energy functionals [19], as well as from DFT specialized for strongly interacting electrons [12].

In this work we present a 2D density functional combining the 2D generalized-gradient approximation [15] (GGA) for the exchange and a local density functional for the correlation [18]. The functional is shown to be accurate not only for the exchange and correlation energies, respectively, but also for the total energy. Thus, it could be readily used for the calculation of, e.g., chemical potentials and addition energies of quantum-dot systems

– quantities directly available from Coulomb-blockade transport experiments [20]. As a numerically efficient method, the functional is also a promising tool for numerical studies on confined quantum Hall systems typically dealt with single-particle theories or with the Thomas-Fermi approximation [21].

2. THEORY

We focus here on the Kohn-Sham (KS) scheme within DFT to obtain the ground-state total energies E_{tot} and densities $n(\mathbf{r})$ of a 2D system containing N Coulomb-interacting electrons. The total energy can be written, in Hartree atomic units, as a density functional

$$E[n] = T_s[n] + E_H[n] + E_{\text{xc}}[n] + \int d^2r v(\mathbf{r})n(\mathbf{r}), \quad (2.1)$$

where $T_s[n]$ is the KS kinetic energy functional, $E_H[n]$ is the Hartree energy, $v(\mathbf{r})$ is the external scalar potential, and $E_{\text{xc}}[n]$ is the exchange-correlation energy functional. The latter can be decomposed into the exchange and correlation parts as $E_{\text{xc}}[n] = E_x[n] + E_c[n]$. In the following sections we consider approximations for these parts separately.

It should be noted that for $E_x[n]$ we use an approximation which depends on the spin density and thus also applies to spin-polarized states within the spin-DFT formalism, whereas for $E_c[n]$ the approximation depends only the total density, and its derivation suggests that is suited for spin-unpolarized systems. This restriction for the correlation calls for a spin-dependent extension.

2.1. Exchange

The following 2D-GGA is based on the idea of Becke [22, 23] for 3D systems, which was extended to 2D in Ref. [15]. The spin-density (n_σ) functional for the exchange energy can be expressed as

$$E_x[n_\sigma] = -\pi \sum_{\sigma=\uparrow,\downarrow} \int d^2r n_\sigma(\mathbf{r}) \int ds \bar{h}_{x,\sigma}(\mathbf{r}, s), \quad (2.2)$$

where $\bar{h}_{x,\sigma}(\mathbf{r}, s)$ is the *cylindrical average* with respect to $\mathbf{s} = \mathbf{r}' - \mathbf{r}$ (with $s = |\mathbf{r}' - \mathbf{r}|$) of the exchange-hole (or Fermi-hole) function $h_{x,\sigma}(\mathbf{r}, \mathbf{r}')$ around the reference point \mathbf{r} . Note that here we use a definition of the exchange energy for which the corresponding hole function

is positively defined. The Taylor expansion of $\bar{h}_{x,\sigma}(\mathbf{r}, s)$ with respect to s up to the second order gives

$$\bar{h}_{x,\sigma}(\mathbf{r}, s) = n_\sigma(\mathbf{r}) + C_x^\sigma(\mathbf{r})s^2 + \dots, \quad (2.3)$$

where

$$C_x^\sigma(\mathbf{r}) = \frac{1}{4} \left[\nabla^2 n_\sigma(\mathbf{r}) - 2\tau_\sigma(\mathbf{r}) + \frac{1}{2} \frac{|\nabla n_\sigma(\mathbf{r})|^2}{n_\sigma} + 2 \frac{\mathbf{j}_{p,\sigma}^2(\mathbf{r})}{n_\sigma(\mathbf{r})} \right] \quad (2.4)$$

is the local curvature of the exchange hole around the given reference point \mathbf{r} [14, 22, 24, 25]. Here τ_σ is twice the kinetic-energy density and $\mathbf{j}_{p,\sigma}$ is the paramagnetic current density.

In the small density-gradient limit (SGL), we take the homogeneous 2D electron gas (2DEG) as the reference system. When the inhomogeneity is small, we may write

$$\bar{h}_{x,\sigma}(\mathbf{r}, s) = \begin{cases} [1 + a_\sigma(\mathbf{r})s^2 + b_\sigma(\mathbf{r})s^4 + \dots] \bar{h}_{x,\sigma}^{2\text{DEG}}(s), & \text{if } k_{F,\sigma}s < z \\ \bar{h}_{x,\sigma}^{2\text{DEG}}(s), & \text{if } k_{F,\sigma}s \geq z. \end{cases} \quad (2.5)$$

Here $\bar{h}_{x,\sigma}^{2\text{DEG}}$ is the exact exchange-hole function for the 2DEG [26], $k_{F,\sigma} = \sqrt{4\pi n_\sigma}$ is the 2D Fermi momentum, and where z is the first zero of J_1 , i.e., the Bessel function of the first kind appearing in $\bar{h}_{x,\sigma}^{2\text{DEG}}$. Comparing Eqs. (2.3) and (2.5), using the 2D Thomas-Fermi expression for τ_σ , and enforcing the exact normalization of $\bar{h}_{x,\sigma}$ lead to expressions for a_σ and b_σ (see Ref. [15] for details), and finally the SGL can be written as

$$E_{x,\sigma}^{\text{SGL}} = -\frac{5}{48\sqrt{\pi}} \left[\frac{I(0)I(3) - I(1)I(2)}{I(3)} \right] \int d^2r \frac{|\nabla n_\sigma(\mathbf{r})|^2}{n_\sigma^{3/2}(\mathbf{r})}, \quad (2.6)$$

where

$$I(m) = \int_0^z dy y^m J_1^2(y). \quad (2.7)$$

In the large density-gradient limit (LGL) the *density gradient* dominates over the other terms in $\bar{h}_{x,\sigma}$, and, secondly, the exchange hole vanishes at large s following a decay function denoted here as F . Thus, we may write

$$\bar{h}_{x,\sigma}(\mathbf{r}, s) \approx \left[\frac{1}{8} \frac{|\nabla n_\sigma(\mathbf{r})|^2}{n_\sigma(\mathbf{r})} s^2 \right] F(\alpha_\sigma(\mathbf{r}) s), \quad (2.8)$$

where $F(y) = e^{-y^2}$ corresponds to a Gaussian approximation for the exchange hole. The parameter α_σ can be determined by enforcing again the exact normalization constraint for $\bar{h}_{x,\sigma}$. The resulting expression for the LGL of the exchange energy in Eq. (2.2) is

$$E_{x,\sigma}^{\text{LGL}} = -\frac{\pi^{1/4}}{2^{3/2}} G(2) G^{-3/4}(3) \int d^2r \frac{|\nabla n_\sigma(\mathbf{r})|^{1/2}}{n_\sigma^{3/4}(\mathbf{r})}, \quad (2.9)$$

where

$$G(m) = \int_0^\infty dy y^m e^{-y^2}. \quad (2.10)$$

Finally we interpolate the results for the SGL [Eq. (2.6)] and LGL [Eq. (2.9)] leading to the 2D-GGA expression for the exchange energy,

$$E_x^{\text{GGA}}[n_\sigma, \nabla n_\sigma] = E_x^{\text{LDA}}[n_\sigma] - \zeta \sum_{\sigma=\uparrow,\downarrow} \int d^2r \frac{|\nabla n_\sigma(\mathbf{r})|^2}{n_\sigma^{3/2}(\mathbf{r}) \left[1 + \gamma \frac{|\nabla n_\sigma(\mathbf{r})|^2}{n_\sigma^3(\mathbf{r})}\right]^{3/4}}, \quad (2.11)$$

where

$$E_x^{\text{LDA}}[n_\sigma] = -\frac{8}{3\sqrt{\pi}} \int d^2r n_\sigma^{3/2}(\mathbf{r}) \quad (2.12)$$

is the 2D-LDA exchange energy. The parameters ζ and γ are fitted to a set of parabolic quantum dots yielding $\zeta = 0.003317$ and $\gamma = 0.008323$ [15]. Interestingly, these values are close to the parameters found by Becke by fitting a series of noble-gas atoms [23].

2.2. Correlation

Here we review the derivation of the correlation energy functional presented in Ref. [18]. The correlation energy can be expressed as [18, 27, 28]

$$E_c = \int d^2r \int d^2s n_{2,\text{SD}}(\mathbf{r}, \mathbf{s}) \frac{\varphi^2(\mathbf{r}, \mathbf{s}) - 2\varphi(\mathbf{r}, \mathbf{s})}{s}, \quad (2.13)$$

where $n_{2,\text{SD}}(\mathbf{r}, \mathbf{s})$ is the pair density calculated using a single Slater determinant (SD) generated within DFT from the occupied KS orbitals [see Eqs. (2.15) and (3.1) below]. Further, the quantity

$$\varphi(\mathbf{r}, \mathbf{s}) = [1 - \Phi(\mathbf{r})(1 + \alpha s)] e^{-\beta^2(\mathbf{r})s^2} \quad (2.14)$$

describes the correlation between electron pairs. Here $\mathbf{s} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{r} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ represent the relative and center-of-mass coordinates of a representative electron pair, respectively. The quantities α , β , and Φ act as correlation factors to be determined as follows.

- First, α can be found by considering the cusp condition for a 2D singlet many-body wavefunction. This corresponds to a situation when two electrons are brought to the same point. Application of the exact result of Rajagopal *et al.* [29] to the model wave function

$$\Psi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) = \Psi_{\text{SD}}(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) \prod_{i<j} [1 - \varphi(\mathbf{r}_i, \mathbf{r}_j)] \quad (2.15)$$

– from which the correlation energy given in Eq. (2.13) is obtained [18] – yields $\alpha = 1$.

- Second, we introduce β as a *local* quantity determining the local correlation length. We can estimate this length by comparing the "correlation area", i.e., area integral over the exponential part of Eq. (2.14), to the area of a circle enclosing, on the average, one electron, i.e., πr_s^2 , where $r_s(\mathbf{r}) = 1/\sqrt{\pi n(\mathbf{r})}$. The comparison yields $\beta(\mathbf{r}) = q\sqrt{n(\mathbf{r})}$, where we introduce q as a fitting parameter.
- Third, the integral of $\varphi(\mathbf{r}, \mathbf{s})$ [Eq. (2.14)] over the relative coordinate \mathbf{s} must vanish (see Refs. [28, 30] for details). This leads to a relation $\Phi(\mathbf{r}) = \beta(\mathbf{r})/[\beta(\mathbf{r}) + \sqrt{\pi}/2]$.

To further simplify the expression for the correlation energy [Eq. (2.13)], we use a Gaussian approximation [30, 31] for the SD pair density,

$$n_{2,\text{SD}}(\mathbf{r}, \mathbf{s}) = n_{2,\text{SD}}(\mathbf{r}) e^{-s^2/\gamma^2(\mathbf{r})}. \quad (2.16)$$

Applying the exact sum rule on the pair density yields

$$n_{\text{SD}}(\mathbf{r}) = \frac{2}{N-1} \int d^2s \, n_{2,\text{SD}}(\mathbf{r}, \mathbf{s}) = \frac{2\pi}{N-1} n_{2,\text{SD}}(\mathbf{r}) \gamma^2(\mathbf{r}), \quad (2.17)$$

where we can use the well-known relation in the SD case: $n_{2,\text{SD}}(\mathbf{r}) = \frac{1}{4}n_{\text{SD}}^2(\mathbf{r})$. Further, we can associate the SD density n_{SD} with the density in the second item of the list above. Taken together, and performing the integration over s in Eq. (2.13), leads to the correlation energy

$$E_c[n] = \int d^2r \, n(\mathbf{r}) \epsilon_c(\mathbf{r}), \quad (2.18)$$

where $\epsilon_c(\mathbf{r})$ is the local correlation energy per electron having an expression

$$\begin{aligned} \epsilon_c(\mathbf{r}) = \frac{\pi}{2q^2} \left\{ \frac{\sqrt{\pi} \beta(\mathbf{r})}{2\sqrt{2+c}} [\Phi(\mathbf{r}) - 1] + \frac{\Phi(\mathbf{r})[\Phi(\mathbf{r}) - 1]}{2+c} \right. \\ \left. + \frac{\sqrt{\pi} \Phi^2(\mathbf{r})}{4\beta(\mathbf{r})(2+c)^{3/2}} + \frac{\sqrt{\pi} \beta(\mathbf{r})}{\sqrt{1+c}} [\Phi(\mathbf{r}) - 1] + \frac{\Phi(\mathbf{r})}{1+c} \right\}, \end{aligned} \quad (2.19)$$

with $c = \pi/[2(N-1)q^2]$. We point out that this expression includes an *ad-hoc* modification in the first term, $[\Phi(\mathbf{r}) - 1]^2 \rightarrow [\Phi(\mathbf{r}) - 1]$. This modification is introduced to better reproduce the reference values of numerically accurate correlation energies for a set of quantum dots and the 2DEG [18].

Equation (2.18) with Eq. (2.19) define an explicit density functional for the correlation energy. It is self-interaction free (in the sense that it is equal to zero for one particle systems, $N = 1$) and depends on a single fitting parameter q (see below). We point out that the

functional is not size-consistent due to the nonlinear dependence on N . In practice, however, this does not affect the performance of the approximation when considering finite 2D systems with fixed N , e.g., semiconductor quantum dots.

The fitting parameter $q = 3.9274$ is chosen to reproduce the *exact* correlation energy $E_c = E_{\text{tot}} - E_{\text{tot}}^{\text{EXX}}$ for the singlet state of a two-electron parabolic quantum dot (2D harmonic oscillator) with the confining strength $\omega = 1$. Here $E_{\text{tot}} = 3$ is Taut's analytic result [32] and $E_{\text{tot}}^{\text{EXX}}$ is the exact-exchange result. For consistency, and in order to provide a predictive approximation, the fitting parameter q is then kept fixed for *all* systems.

3. RESULTS

The sum of Eqs. (2.11) and (2.18) is the approximation we employ for the E_{xc} . We test this functional in the calculation of ground-state total energies of spin-unpolarized, closed-shell quantum dots. Thus $n_{\uparrow}(\mathbf{r}) = n_{\downarrow}(\mathbf{r}) = n(\mathbf{r})/2$ and, as a consequence, we can restrict our calculations to the standard DFT scheme. The total energy is then obtained from Eq. (2.1) in connection with solving self-consistently the KS equation

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{KS}}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}). \quad (3.1)$$

The KS potential is given by $v_{\text{KS}}(\mathbf{r}) = v_{\text{H}}(\mathbf{r}) + v_{xc}(\mathbf{r}) + v(\mathbf{r})$, where the Hartree potential is computed as

$$v_{\text{H}}(\mathbf{r}) = \int d^2r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (3.2)$$

the exchange-correlation potential is obtained from

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}, \quad (3.3)$$

and $v(\mathbf{r})$ is the given external potential. The KS orbitals $\varphi_i(\mathbf{r})$ provide the the total density as $n(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2$ ($N/2$ electrons for each spin-channel), and ϵ_i are the corresponding KS energies.

Below, we compare the reference results available from (numerically) exact calculations to self-consistent DFT results obtained using the real-space `octopus` code [33] with the proposed functional and with the LDA, respectively.

TABLE I: Total energies (in atomic units) for parabolic quantum dots. We compare numerically exact results ($E_{\text{tot}}^{\text{ref}}$) to our functional ($E_{\text{tot}}^{\text{here}}$) and to the local-density approximation ($E_{\text{tot}}^{\text{LDA}}$). The last row contains the mean percentage error Δ .

N	ω	$E_{\text{tot}}^{\text{ref}}$	$E_{\text{tot}}^{\text{here}}$	$E_{\text{tot}}^{\text{LDA}}$
2	1	3*	3.026	3.066
2	1/4	0.9324 [†]	0.936	0.952
2	1/6	2/3*	0.668	0.682
2	1/16	0.3031 [†]	0.300	0.308
6	1/1.89 ²	7.6001 [‡]	7.629	7.632
6	1/4	6.995 [†]	7.009	7.012
6	1/16	2.528 [†]	2.528	2.534
12	1/1.89 ²	25.636 [‡]	25.72	25.67
Δ			0.42%	1.2%

* Analytic solution by Taut from Ref. 32. [†] CI data from Ref. 34. [‡] Diffusion QMC data from Ref. 35.

3.1. Parabolic quantum dots

First we consider a set of 2D parabolic (harmonic) quantum dots, where the external confining potential in Eq. (2.1) is given by $v(r) = \omega^2 r^2/2$. Table I shows the total energies for $N = 2 \dots 12$ with various confinement strengths ω . The reference data $E_{\text{tot}}^{\text{ref}}$ have been collected from analytic results by Taut [32], configuration-interaction calculations by Rontani *et al.* [34], and diffusion quantum Monte Carlo (QMC) calculations by Pederiva *et al.* [35]. Overall, both LDA and our functional perform very well with respect to the reference data, the mean percentage errors being $\sim 1.2\%$ and 0.42% , respectively. However, in view of the excellent performance of the LDA in terms of total energies, it is remarkable that the present functional reduces the error further by a factor of three. Moreover, it should be noted that the LDA total energy has the well-known error compensation from exchange and correlation energies, respectively [10]. In the results shown in Table I, for example, the LDA overestimates (underestimates) the exchange (correlation) energy by $10 \dots 20\%$, whereas the corresponding errors in our functional are significantly smaller [15, 18].

As seen in Table I, the total energy of the largest system with $N = 12$ is obtained by the LDA more accurately than by our functional. This raises a question whether the LDA would considerably outperform our functional in the important large- N limit. Therefore, we also tested the filling-factor $\nu = 2$ state of a $N = 48$ quantum dot, for which relatively accurate variational QMC data is available (see Fig. 8 in Ref. [36]). Remarkably, the relative errors of the present functional and the LDA are only $\sim 0.1\%$ (note that in Ref. [36] a different DFT code was used producing a slightly larger error in the LDA). This test confirms that the present functional is valid also in relatively large 2D systems. This is expected in view of the good reproducibility of the 2DEG result imposed on both the exchange [see Eq. (2.5)] and correlation (see Fig. 1 in Ref. [18]).

3.2. Rectangular quantum dots

Next we consider the total energies of rectangular quantum dots with a side-length ratio χ and a total area of π^2 (a.u.) enclosed by hard-wall boundaries. As the reference results we use the variational QMC data in Ref. [37], where the choice for the dot area was motivated by a rational-valued single-electron energy spectrum, $E_{ij} = (\chi i + j/\chi)/2$, where $(i, j) = 1, 2, 3, \dots$. Moreover, the dot size corresponds to an realistic area of $\sim 900 \text{ nm}^2$, when using the effective-mass approximation for electrons in GaAs [37].

The total-energy results are shown in Table II. Again, the present functional is more accurate than the LDA: in this case the LDA error is reduced by a factor of 1.7. There is no clear tendency in the accuracies as a function of N . Precise determination of the N -dependence would require highly accurate numerical calculations and reference data. In this respect the present boundary conditions (hard walls) are problematic due to the huge number of grid points needed.

4. SUMMARY

We have considered a practical and accurate density functional for the energy of electrons confined in two dimensions. The exchange contribution is a semi-local generalized-gradient approximation, and the correlation part has been built on the Colle-Salvetti scheme with a Gaussian approximation for the pair density. We have verified that self-consistent appli-

TABLE II: Total energies (in atomic units) for rectangular quantum dots with a total area of π^2 and side-length ratio χ . We compare numerically accurate quantum Monte Carlo results [37] ($E_{\text{tot}}^{\text{ref}}$) to our functional ($E_{\text{tot}}^{\text{here}}$) and to the local-density approximation ($E_{\text{tot}}^{\text{LDA}}$). The last row contains the mean percentage error Δ .

χ	N	$E_{\text{tot}}^{\text{ref}}$	$E_{\text{tot}}^{\text{here}}$	$E_{\text{tot}}^{\text{LDA}}$
1	2	3.273	3.312	3.357
	6	26.97	26.98	27.10
	8	46.79	46.86	46.99
	12	103.34	103.1	103.2
	16	178.50	178.4	178.5
2	2	3.696	3.674	3.735
	4	12.32	12.36	12.45
	6	27.15	27.25	27.36
	8	47.82	47.69	47.80
	12	102.26	102.1	102.2
	16	177.80	178.0	178.1
3	2	4.375	4.321	4.403
	4	12.99	12.95	13.08
	6	26.69	26.75	26.91
	8	46.35	46.49	46.67
	12	103.46	103.4	103.5
	16	177.37	177.1	177.3
Δ			0.34%	0.57%

cation performs very well for a variety of two-dimensional quantum-dot systems. On the average, the present functional was found to considerably reduce the error in total energies over the local-density approximation. Preliminary tests suggest also good performance for large electron numbers with a modest computational cost. Future developments include an extension of the correlation part to spin-polarized systems.

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